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AMENDED SPECIFICATION

Reprinted as amended under Section 8 of the Patents and Designs Acts, 1907 to 1932.

PATENT SPECIFICATION

Application Date: March 4, 1935. No. 6747/35. **453,203**

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(A Sample has been furnished in this case under Section 2, sub-section 5, of the Patents and Designs Acts, 1907 to 1932).

COMPLETE SPECIFICATION

Improvements in Plastics

I, WERNER WILFRED DUECKER, of 198, Dewey Street, Edgewood, Allegheny County, Pennsylvania, United States of America, a Citizen of the United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement :—

This invention relates to the treatment of sulphur to modify the crystallising habit of the sulphur and obtain a product that will continue for relatively long periods of time or perhaps permanently, in non-crystalline condition; and a product, furthermore, that will be of plastic nature. Earlier discovery reveals the fact that the introduction of certain organic and inorganic sulphides into sulphur results in a product that mainfests in less degree, or not at all, the crystallising habit of sulphur alone, and a product that, additionally, is plastic, and it is the object of the invention to provide an improved method of preparing this product.

The organic sulphides that here are contemplated comprise those commonly produced by the interaction of polysulphides or sulphur with olefinic compounds containing the group C_nH_{2n} combined with a negative radical. These products have amorphous characteristics. Typical of them is the product of the reaction of calcium or sodium polysulphide with ethylene dichloride. It is a plastic, rubber-like mass, containing generally 82% sulphur, 15.5% carbon, and 2.5% hydrogen. The structure is unknown, but the substance is recognised to be, generally speaking, an organic sulphide or with greater likelihood, a polymerization product of an organic sulphide or of a mixture of organic sulphides. This rubber-like mass, although it will soften as it is heated, manifests no definite melting point, and it may not be brought by melting to fluid consistency. It is a product now on the market and because of the properties indicated it is represented to be of peculiar value.

When this product is dissolved in sulphur, the solution has properties and characteristics which neither component alone possesses and which make the solution available for new uses. Unlike sulphur, it will continue indefinitely in non-crystalline condition; unlike the sulphide alone, it has a definite melting point and, accordingly, the very valuable characteristic that in liquid condition it may be caused to penetrate narrow interstices and may be used as a substance with which to impregnate other bodies. Furthermore, since sulphur is relatively cheap, the solution of the invention is less expensive than the sulphide alone.

According to the invention the method of preparing a solution of the organic sulphide in sulphur consists in maintaining a body of molten sulphur at a temperature not exceeding 160° C., and causing an aliphatic unsaturated hydrocarbon in gaseous condition to bubble through the sulphur, whereby the hydrocarbon, taking on sulphur, will form sulphide, and the sulphide without break in the carbon chain, will go into solution in the excess sulphur.

The reaction is maintained, with stirring if need be, until the mass is homogeneous. It may then be cooled, and is then serviceable.

In carrying the invention into effect, an olefine gas, for example, ethylene, is caused to bubble through a bath of molten sulphur maintained at a temperature not exceeding 160° C., and preferably between 140° and 160° C., an olefine sulphide being formed which goes straight into solution in the sulphur.

The reaction may be assisted by the

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presence of a catalyst in the form of an inorganic sulphide, such as copper sulphide, or an organic sulphide such as the mercaptans.

The temperature limitation is important. The temperature being maintained above the melting point of sulphur, and yet not more than 160° C., the reaction is not attended (as occurs if the bath of sulphur be of higher temperature) with release of hydrogen sulphide gas—at least not in any appreciable amount. The significance of this is that the polymers of the olefine sulphides are not broken down. The chain of the olefine molecules takes on sulphur, without a breaking of the chain. The result is a plastic substance. If operation were conducted at higher temperature characterised by release of hydrogen sulphide (which means the breaking of the molecular chain), the resulting product would be crystalline, and not plastic, and it is the plastic product that has utility within the contemplation of this invention.

The olefine gas may be in pure or substantially pure state, or it may be introduced into the molten sulphur in such diluted state or condition as may be found practical and convenient. Still gas—that is to say, gas from a petroleum refinery which is essentially olefine gas diluted with carbon dioxide and other adulterants is serviceable in the practice of the invention by virtue of its essential olefine content.

And similarly as olefine gas is serviceable so other unsaturated aliphatic hydrocarbons in gaseous state are serviceable, acetylene for example. And, the sulphur being maintained at a temperature exceeding its own melting point but not at a temperature so high as to effect the breaking down of the derivative products, with the release of hydrogen sulphide gas, the same reaction will occur; the unsaturated hydrocarbon will take up sulphur and the carbon chain remaining unbroken, the so derived sulphide will go into solution in the excess molten sulphur.

The reaction that occurs is distinguished from the reaction that would occur were the temperature higher, in that it is a reaction of addition, and not a reaction of substitution.

The reaction may be accelerated by the presence of any of the following substances, namely, the chlorinated diphenyls, chlorinated naphthalenes, phenol-sulphur chloride resins, camphor and diphenyl guanidine (D.P.G.).

The various organic sulphides that have been characterised and described may be formed within and dissolved in sulphur in all proportions. The mass resulting from the mixture varies in viscosity, according to the value of the sulphide content. When cold also, the properties of the mass depend upon the value of the sulphide content. In general, all such mixtures are plastic. Since the sulphide itself is a very viscous plastic material, it has the effect of delaying the crystallization of the sulphur. To what extent crystallization is delayed or suspended depends upon the value of the sulphide content. Solutions that contain less than 7% of sulphide possess a certain plasticity. Such solutions are, however, difficult to sheet on a rubber mill. Solutions that contain more than 7% of sulphide may be sheeted quite readily on the rubber rolls. By varying the sulphide content, masses can be produced that are hard and semi-plastic, and others that are soft and flexible.

These masses differ from both components. Sulphur is brittle, hard, and crystalline. These solutions may be soft, semi-plastic, and practically non-crystalline. The sulphide alone is amorphous, flexible, and resembles rubber. That the mass is indeed a solution is evidenced by the fact that from it the sulphur may be extracted again.

The solution, plastic as the dissolved sulphide is plastic, has the added characteristic that it can be melted. The sulphide alone is a relatively expensive material. The cost of the solution is much less.

Of the "accelerators" previously mentioned, the chlorinated diphenyls, chlorinated naphthalenes, phenol-sulphur chloride resins and diphenyl guanidine also have the property of modifying the physical characteritics of the solution. Other substances which may be used as modifying agents are cotton seed oil, vegetable oils, asphalt or ozokerite or the sulphides produced by the reaction of china wood oil or oleic acid with sulphur. Generally these substances impart waxy characteristics to the solution with the exception of diphenyl guanidine which makes the solution slightly more crystalline. The quantities of these materials required to modify the properties of the solution may vary, but generally do not exceed 0.5%.

The usefulness of these solutions are many, as such solutions can be produced with variety of physical characteristics. They may be extruded into various shapes and forms. They may be used to impregnate cellulosic materials, fabrics, cement, stone, etc. They may be used as thin coating films.

They resist abrasion, and can be used to cover materials which are subjected to abrasive influence.

They can be used as bonding agents, in bonding felt to metal, and in bonding various other bodies.

They can be used to line pickling vats, electrolytic cells, acid tanks, and surfaces that come in contact with corrosive salt solutions.

One of their principal uses is the impregnation of fabrics, etc., for the construction of hose, etc., useful in the conveyance of acids, hydrocarbons, corrosive salt solutions, and in the fabrication of flexible ventilators such as are used in mines, etc., packing materials, and flexible diaphragms.

Because such products are flexible, they may be used as substitutes for rubber. They are also valuable as insulating materials.

A sample of a plastic body produced in accordance with the following example has been furnished under Section 2 (5) of the Patents and Designs Acts 1907—32.

"Sixty five grams of sulphur were heated in an oil bath to a temperature of 133—137° C. Through the sulphur so rendered molten thirty-two grams of acetylene gas were passed in the course of a period of thirty hours. The gas was bubbled through the molten sulphur at a rate of about fourteen cubic centimetres per minute. After all the gas had been passed through the sulphur the reaction mixture was allowed to cool. The unreacted sulphur was then dissolved in carbon disulphide, and the insoluble rubbery reaction product was filtered off.

I am aware that the specification of my prior Patent No. 453202 relating to the manufacture of sulphur cements describes the preparation of a solution of an olefine sulphide in sulphur by passing a gaseous olefine through molten sulphur at a temperature not exceeding 160° C. and I wish it to be understood that I make no claim in the present specification to anything claimed in my prior specification.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that subject to the foregoing disclaimer, what I claim is:—

1. The method herein described of preparing a solution of an organic sulphide in sulphur which consists in maintaining a body of molten sulphur at a temperature not exceeding 160° C., and causing an aliphatic unsaturated hydrocarbon in gaseous condition to bubble through the sulphur, whereby the hydrocarbon, taking on sulphur, will form sulphide, and the sulphide, without break in the carbon chain, will go into solution in the excess sulphur.

2. The method herein described of preparing a solution of an olefine sulphide in sulphur which consists in bringing a body of sulphur to molten condition, and to a temperature not exceeding 160° C., and causing an olefine in gaseous condition to ~~bubble~~ through the bath of molten sulphur, whereby a portion of the sulphur will be ~~altered~~ to an olefine sulphide which goes into solution in the excess sulphur.

3. The method according to claim 1 or 2 wherein the reaction is carried out in the presence of an accelerator of the group herein set forth.

4. The method according to claim 1, 2 or 3, wherein the reaction is carried out in the presence of a modifying agent of the group herein set forth.

Dated this 4th day of March, 1935.

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